Final Report

SOURCES, ABUNDANCE, AND FATE
OF GASEOUS ATMOSPHERIC POLLUTANTS

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I   INTRODUCTION

It is a popular misconception that almost everything present in the earth's atmosphere, except nitrogen, oxygen, and a few inert rare gases, is an air pollutant or the remnant of pollution activities. This is not the case. There are sources in the natural environment of a wide variety of gaseous and particulate materials which are commonly classed as air pollutants when they are emitted by man-made sources. In addition, the atmosphere possesses a number of mechanisms which act to remove, sometimes at a quite rapid rate, most if not all of the materials emitted into it.

It is, of course, also obvious that while these atmospheric scavenging mechanisms are quite effective they can be overburdened by excessive emissions occurring in relatively short periods of time or in limited geographical areas. The gradual accumulation of carbon dioxide in the atmosphere is a case where the available environmental scavenging mechanisms are significantly lagging the pollutant emission rate. On a much smaller scale, the air pollution problems in major urban areas are examples of situations where the pollutant emission rate seriously overburdens the scavenging processes for significant but limited periods of time within the confines of the urban area.

The topic of this report, the atmospheric cycles of trace chemicals including but not being restricted to air pollutants, is one that has rarely received detailed consideration. Instead it often seems to be tacitly assumed that pollutants once released into the atmosphere will disappear as soon as the air mass moves across the city boundary. It is also often assumed, apparently, that commonly identified pollutants are uniquely related to man's activity and that pollutant emissions constitute

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a permanent and ever-worsening burden for our atmospheric environment. These assumptions are drastic oversimplifications and can lead their proponents far from reality.

It is the purpose of this report to examine our present state of knowledge of the atmospheric cycles followed by a variety of common gaseou materials. This will be done by analyzing the major natural and urban pollution sources, estimating the effectiveness of applicable atmospheric reaction processes, and determining the effectiveness of the processes by which the material is finally removed from the atmosphere. It will be apparent that our knowledge of these atmospheric processes is, in many cases, fragmentary. Where this is the case, further research is called for and will be pointed out.

Sources of the various materials have been estimated from the available literature, but a detailed intercomparison of source data has not been undertaken because a detailed "emissions inventory" was not within the scope of this program. In general, the magnitudes of the various pollutant sources can be estimated reasonably well while the possible natural sources can only be crudely defined.

We have in a general sense divorced our considerations from a detail reporting and analysis of conditions within specific urban areas and fro studies which report the periodic "highest-ever" type of statistics. Th total atmospheric system is so much greater than the polluted envelope o any one city that the transient effects noted in a given area are important to our study only to the degree that they indicate sources of pollu tants that can affect the atmospheric system.

In many ways this study is a first effort at solving the problem of the integrated effects of natural and urban emanations in the atmosphere Progress has been made here, but more needs to be done.

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II SUMMARY AND CONCLUSIONS

A. Summary

This analysis of the sources, abundance, and fate of gaseous atmos-
pheric pollutants has considered three families of compounds--sulfurous,
nitrogenous, and organic; and two inorganic carbon compounds--carbon
monoxide and carbon dioxide. With the exception of CO_2, we have followed
similar patterns in our analyses of these materials and have produced
rather detailed analyses. The presentation of CO_2 is only a brief review
of the current state of thinking.

This analysis has included estimates of annual world-wide emissions
of pollutants: SO_2, H_2S, CO, NO_2, NH_3, and organics. The magnitudes of
the natural emanations of a variety of materials have also been considered,
although we must admit that the means of estimating these emissions are
very crude because so little study has been made of emissions from other
than urban air pollution sources. The following paragraphs give the high-
lights of our analyses.

1. Sulfur Compounds

Sulfur compounds, in the form of SO_2, are currently the most topical
of the numerous air pollutants. Sulfur enters the atmosphere as air pol-
lutants in the form of SO_2, H_2S, H_2SO_4, and particulate sulfates; and as
natural emanations in the form of H_2S and sulfates. On an annual basis,
the tonnage of sulfur which is discharged into the atmosphere amounts to
220×10^6 tons. Of this sulfur, about one third comes from air pollution
sources, mostly in the form of SO_2, and the rest comes from natural proc-
esses. It is estimated that H_2S from natural processes accounts for
almost one half of the total sulfur released to the atmosphere, 100×10^6
out of the 220×10^6 tons.

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5. Carbon Dioxide

A brief review of our present understanding of CO_2 in the atmosphere indicates that here we have a clear example of a situation where pollutant emissions are significant enough to cause measurable changes in the ambient concentrations. Measured increases in CO_2 in the atmosphere are about 0.06 ppm per month. If CO_2 levels continue to rise at present rates, it is likely that noticeable increases in temperature could occur. Changes in temperature on a world-wide scale could cause major changes in the earth's environment over the next several hundred years including changes in the polar ice caps.

It seems ironic that given this picture of the likely result of massive CO_2 emissions so little concern is given to CO_2 as an important air pollutant.

B. Conclusions

Important factors resulting from our analysis of atmospheric trace components and pollutants are summarized in Table I. This table indicates the nature and size of the natural and pollutant sources, the estimated concentrations in the ambient atmosphere, probable scavenging reactions, estimated residence times, and the most important references which pertain to these various materials. This tabulation is, of course, amplified in the main body of this report.

In our discussions of atmospheric residence times for the various materials we have considered, it seems that the residence times seem to be either a few days or a few years. In the "few days" classification the more reactive gases: SO_2, H_2S, NO, NO_2, and NH_3. In the longer "few years" classification are the significantly less reactive materials: CO, N_2O, CH_4, and CO_2. In the case of the more reactive gases the tropospheric scavenging and reaction processes are relatively well known and include photochemical, homogeneous, and heterogeneous reactions. For the latter

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SUMMARY OF SOURCES, CONCENTRATIONS, AND MAJOR REACTIONS OF ATMOSPHERIC TRACE GASES

CONTAMINANT	MAJOR POLLUTION SOURCES	NATURAL SOURCES	ESTIMATED EMISSIONS		ATMOSPHERIC BACKGROUND CONCENTRATIONS	CALCULATED ATMOSPHERIC RESIDENCE TIME	REMOVAL REACTIONS AND SINKS	PRINCIPAL REFERENCES	REMARKS
			Pollution	Natural					
SO_2	Combustion of coal and oil	Volcanoes	146×10^6 tons	None	0.2 ppb	4 days	Oxidation to sulfate by ozone or after absorption by solid and liquid aerosols	Eriksson (1959, 1960, 1963), Junge (1963), Lodge and Pate (1966)	Photochemical oxidation with NO_2 and HC may be the process needed to give rapid transformation of $SO_2 \rightarrow SO_4$
H_2S	Chemical processes, sewage treatment	Volcanoes, biological action in swamp areas	3×10^6 tons	100×10^6 tons	0.2 ppb	2 days	Oxidation to SO_2	Junge (1963), Smith et al. (1961)	Only one set of background concentrations available
CO	Auto exhaust and other combustion	Forest fires	220×10^6 tons	11×10^6 tons	0.1 ppm	<3 yr	None known, but large sink necessary	Bates and Witherspoon (1952), SRI Project Reports	
NO NO2	Combustion	Bacterial action in soil (?)	53×10^6 tons	500×10^6 tons	1 ppb	5 days	Oxidation to nitrate after sorption by solid and liquid aerosols, hydrocarbon photochemical reactions	Junge (1963), Leighton (1961), Lodge and Pate (1966)	Very little work done on natural processes
NH_3	Waste treatment	Biological decay	4×10^6 tons	5900×10^6 tons	6 ppb to 20 ppb	2 days	Reaction with SO_2 to form $(NH_4)_2SO_4$, oxidation to NO_3 nitrate	Eriksson (1952), Georgii (1963), Junge (1963), Lodge and Pate (1966)	No quantitative rate data on oxidation of NH_3 to NO_3 which seems to be dominant process in atmosphere
N_2O	None	Biological action in soil	None	1000×10^6 tons	0.25 ppm	1-3 yr	Photo dissociation in stratosphere, biological action in soil	Bates and Hays (1967)	No information on proposed absorption of N_2O by vegetation
Hydrocarbons	Combustion exhaust, chemical processes	Biological processes	88×10^6 tons	480×10^6 tons	CH_4: 1.5 ppm, non CH_4: <1 ppb	16 yr (CH_4)	Photochemical reaction with NO/NO_2, O_3; large sink necessary for CH_4	Bates and Witherspoon (1952), Ehhalt (1967), Koyama (1963), SRI Project Reports	"Reactive" hydrocarbon emission from pollution = 27×10^6 tons
CO_2	Combustion	Biological decay, release from oceans	1.3×10^{10} tons	10^{12} tons	320 ppm	4 yr	Biological absorption and photosynthesis, absorption in oceans	Revelle (1965)	Atmospheric concentrations increasing by 0.06 ppm per month

materials, our low reactivity class, we postulate that the controlling scavenging process is in the biosphere and that the absorption and react: for CO, CH_4, and N_2O are generally parallel to the CO_2 absorption and photosynthesis process. Although this is only speculation at this time, our available facts, in general, support such an argument. For example, the calculated residence time for CO requires a tropospheric scavenging mechanism, and the biosphere is apparently the most logical one availabl. A similar argument holds for CH_4, although the magnitude of the natural source is less well documented. For N_2O, a relatively short resident ti of about four years would reconcile estimates of the likely rate of emis sion from the soil and the much slower photochemical dissociation of N_2O in the stratosphere. We believe that the absorption processes which can occur within the respiration cycle of vegetation will establish upper limits for the residence times of these less-reactive gases and that the residence times will be of the same order as for CO_2, i.e., a few years.

The atmosphere and our environment obviously hold many secrets, including many things that we would like to know about the trace gases i the troposphere. It will require a considerable amount of research to expand our knowledge in this area because it will be necessary to deal with large areas of the world and relatively small concentrations of material. However, this study of the unpolluted, ambient atmosphere mus be an integral part of our program of air pollution research. Otherwise we will be looking at only a very small part of our total environment ar will have no knowledge of when concentrations are reaching a critical s Thus too small a scope in environmental pollution studies will fail to provide a useful early warning of changing conditions.

VII   CARBON DIOXIDE IN THE ATMOSPHERE

The most commonly emitted air pollutant is carbon dioxide, CO_2. In
fact it is so common and such an integral part of all our activities that
air pollution regulations typically specify that CO_2 emissions are not to
be considered as pollutants. This is perhaps fortunate for our present
mode of living, centered as it is around carbon combustion. However,
this seeming necessity, the CO_2 emission, is the only air pollutant which
has been proven to be of global importance to man's environment on the
basis of a long period of scientific investigation. Because of this
obvious relation we believe that any discussion of atmospheric pollutants
should also include a discussion of CO_2, and therefore we have added this
brief summary. This discussion is based on the summary article "Atmos-
pheric Carbon Dioxide," prepared for the Environmental Pollution Panel,
President's Science Advisory Committee, by a committee headed by Dr. Roger
Revelle (Revelle et al., 1965). Unless otherwise referenced the facts
presented here come from this source.

The possibility that changes in atmospheric CO_2 could change world
climate is not a new idea. It was first proposed independently in America
by Chamberlain in 1899 and in Sweden by S. Arrhenius in 1903. Since then
it has been the source of much discussion and investigation, and while we
know a great deal more about the problem, we still cannot quantitatively
evaluate the impact of the accumulation of CO_2 in the atmosphere in terms
of climatic change.

A.   Changes in Atmospheric Carbon Dioxide

The basic problem involved with CO_2 in the atmosphere is that in our
use of fossil fuel we are putting back into the atmosphere as CO_2 within

a relatively short period of time, a few hundred years, a significant part of the carbon which was extracted by plants and buried by rock sediments over a period of half a billion years. The natural scavenging processes for removing CO_2 from the atmosphere are not sufficient to maintain a stable equilibrium in the atmosphere in the presence of this increase in emissions.

Between 1860 and 1940 the consumption of fossil fuel accounted for the release to the atmosphere of an amount of CO_2 equivalent to 7.9% of the total amount of CO_2 in the 1860 ambient atmosphere. By 1950, the added CO_2 amounted to 10.3%; by 1959, 13.8%; and by 1962, 15.2%. During this latter period careful measurements of CO_2 were made on Mauna Loa, Hawaii, and at the South Pole. These two sets of measurements, with an accuracy of about ± 0.1 ppm, permitted an estimate to be made of the secular change in CO_2 in the ambient atmosphere. A plot of these data from Mauna Loa is shown in Fig. 6. The polar and Hawaiian results show without
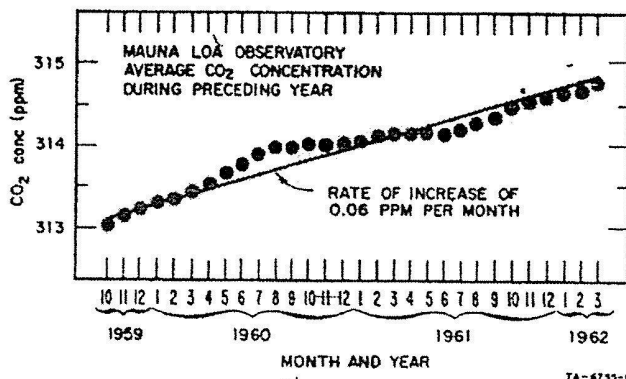
FIG. 6 ANNUAL AVERAGE CO_2 CONCENTRATIONS, MAUNA LOA, HAWAII (Bolin and Keeling, 1963)

any doubt that in the five years between 1958 and 1963, the CO_2 content

of the atmosphere increased by 1.36% for an average increase of 0.23% or

0.06 ppm per month. Fuel emission data show that the CO_2 increase in the

atmosphere in this latest period is just about half the amount of CO_2

released to the atmosphere.

This information can be used to estimate the possible amount of CO_2

which could be emitted to the atmosphere by fuel combustion. Total

recoverable fuels are estimated to be about 10^{12} tons with a CO_2 equiva-

lent of 7.9×10^{18} g or 336% of the 1950 atmospheric CO_2. If, as indica-

ted by the 1958-63 data, half of this stays in the atmosphere, then the

atmospheric CO_2 concentration would increase by almost 170% to about

830 ppm.

The speed with which this change might occur would depend on the rate

of fossil fuel consumption. If the fuel-use growth rate were to remain

at the 1959 rate, 0.35% per year, by the year 2000 the release of CO_2 to

the atmosphere will have increased about 28% above the 1950 amount. How-

ever, if our present trends continue and our use of fuel continues to

expand at about the 5% rate experienced more recently, then the amount of

CO_2 injected into the atmosphere will be about 60% of the 1950 amount.

In these latter two cases, if half the injected CO_2 actually remains in

the atmosphere, in the year 2000 the CO_2 concentrations could be between

14 and 30% higher than in 1950. A consideration of likely world energy

requirements indicates that a 25% increase in CO_2 concentrations is

realistic.

B. Possible Effects of Increased Atmospheric Carbon Dioxide

We are concerned with the possible changes in atmospheric CO_2 content

because CO_2 plays a significant role in establishing the thermal balance

of the earth. This occurs because CO_2 is a strong absorber and back radi-

ator in the infrared portion of the spectrum, especially between 12 and

18 μ. As such CO_2 prevents the loss of considerable heat energy from the earth and radiates it back to the lower atmosphere, the so-called "greenhouse" effect. Thus the major changes which are speculated about as possibly resulting from a change in atmospheric CO_2 are related to a change in the earth's temperature.

The latest data available for estimating CO_2 temperature effects are those of Moller (1963). From Möller's data a CO_2 increase of 25% would result in an increase in temperature at the earth's surface of between 1.1 and 7°F, depending on the assumption made regarding the likely humidity changes accompanying this temperature change. If the amount of water vapor in the atmosphere remained unchanged, the smaller increase would occur, but if the relative humidity were to remain constant then the larger calculated increase would prevail. If, instead of a 25% increase, the CO_2 content were to double, the expected change would be about three times this figure. For atmospheric calculations, Möller's model is still a relatively simple one and has not included all of the possible major interactions occurring in the atmosphere. For this reason it is likely that Möller's calculations overestimate the effects on temperature of an increase in CO_2. More comprehensive models are under development and should be available shortly.

If the earth's temperature increases significantly, a number of events might be expected to occur, including the melting of the Antarctic ice cap, a rise in sea levels, warming of the oceans, and an increase in photosynthesis. The first two items are of course related since the increase in sea level would be mainly due to the added water from the ice cap. Estimates of the possible rate at which the Antarctic ice cap might melt have been made. If the poleward heat flux were increased 10%, the ice cap could disappear in about 4000 years. A shorter time, about 400 years, is estimated if it is considered that half the energy associated with a 2% increase in radiation were used to melt the polar ice cap. A 2% increase might result from a 25% increase in CO_2 by the year 2000.

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With regard to sea level changes, if 1000 years were required to melt the Antarctic ice cap, the resulting 400 foot rise in sea level would occur at a rate of 4 feet per 10 years. This is 100 times greater than presently observed changes.

Changes in ocean temperature would change the distribution of fish and cause a retreat in the polar sea ice. This has happened in recent time on a very limited scale.

Changes in CO_2 might also bring about increased photosynthesis in areas where CO_2 might be a limiting factor in present growth patterns. Where temperature has been a limiting factor to growth and development, an increase in biological activity might be expected.

Although there are other possible sources for the additional CO_2 now being observed in the atmosphere, none seems to fit the presently observed situation as well as the fossil fuel emanation theory.

C. Summary of Carbon Dioxide in the Atmosphere

In summary, Revelle makes the point that man is now engaged in a vast geophysical experiment with his environment, the earth. Significant temperature changes are almost certain to occur by the year 2000 and these could bring about climatic changes.

Since Revelle's report, McCormick and Ludwig (1966) have studied the possible world-wide change of atmospheric fine particles. An increase in fine particulate material will have the effect of increasing the reflectivity of the earth's atmosphere and reducing the amount of radiation received from the sun. Thus this effect would be the opposite of that caused by an increase in CO_2. The argument has been made that the large-scale cooling trend observed in the northern hemisphere since about 1955 is due to the disturbance of the radiation balance by fine particles and that this effect has already reversed any warming trend due to CO_2.

It is clear that we are unsure as to what our long-lived pollutants are doing to our environment; however, there seems to be no doubt that the potential damage to our environment could be severe. Whether one chooses the CO_2 warming theory as described in detail by Revelle and others or the newer cooling prospect indicated by McCormick and Ludwig, the prospect for the future must be of serious concern.

It seems ironic that in our view of air pollution technology we take such a serious concern with small-scale events such as the photochemical reactions of trace concentrations of hydrocarbons, the effect on vegetation of a fraction of a part per million of SO_2, when the abundant pollutants which we generally ignore because they have little local effect, CO_2 and submicron particles, may be the cause of serious world-wide environmental changes.

VIII RESEARCH NEEDS

Earlier in this report we indicated that there are a number of areas where research is vitally needed to increase our knowledge of the specific atmospheric systems. In this section we will briefly describe the more important areas where research is needed.

In the field of sulfur compounds in the atmosphere, the role of H_2S has been postulated as being a major factor. However, we have only one set of ambient background measurements, and thus we know essentially nothing about H_2S in our environment. Vertical concentration gradients for H_2S and SO_2 should be determined to learn more about the ozone oxidation rate of H_2S in the atmosphere. We now believe that aerosol concentration is an important controlling factor as well as ozone concentration, but atmospheric measurements are now necessary to elucidate the real processes and mechanisms of H_2S oxidation in the troposphere. The dry $AgNO_3$ analytical method of Smith, Jenkins, and Cunningworth (1961) should provide an approach of adequate sensitivity for the H_2S measurements. There is also need for better interpretation of atmospheric SO_2 measurements for better understanding of SO_2 oxidation mechanisms.

The delineation of sinks or scavenging mechanisms for CO are a prime need. This should involve studies of possible biological mechanisms in both land and ocean systems. Vertical profiles of CO concentration into the stratosphere would be valuable in trying to understand the circulation of CO through the atmosphere.

The review and analysis which we have made of nitrogen compounds in the ambient atmosphere indicate at least two areas where further work is vital. The possibility of biological or other natural sources of NO in

the ambient atmosphere should be carefully checked, but probably the most important feature as far as atmospheric chemistry is concerned is to determine the source of the nitrate in the atmosphere. The source, on the basis of our analysis of the atmospheric nitrogen cycle, seems to be by the oxidation of NH_3. The oxidation mechanism for atmospheric NH_3 is unknown. This is a very difficult problem which has been evaded or ignored for several years. If NH_3 cannot be shown to be the source of the nitrate, then it will be necessary to find a sufficient natural source of NO or NO_2 to provide the nitrate.

In the area of atmospheric organic gases the almost complete absence of information on all the possible components except CH_4 should be remedied. Proven analytical techniques are available for such studies. While there may be some doubt in the cases of SO_2, H_2S, and other compounds that available techniques are sufficiently sensitive for use in the ambient atmosphere, this is not the case for the low molecular weight organics. Here, gas chromatography is presently capable of detecting the trace levels of many atmospheric organics present in the fractional part-per-billion range. Although the ambient concentrations are known, methane is in the same category as CO in that there is a major need to determine the sink or scavenging mechanism. At present this can only be guessed at.

Past and present studies of CO_2 are detailed and seem to explain adequately the present state of CO_2 in the atmosphere. What is lacking, however, is an application of these atmospheric CO_2 data to air pollution technology and work toward systems in which CO_2 emissions would be brought under control.

Another point which has been made in our discussion is that N_2O, CO, CH_4, and CO_2 have essentially the same atmospheric residence times because, we believe, vegetation plays a major role in the scavenging cycle for each of the materials. This postulate should obviously be carefully checked by

both theoretical and experimental studies. If our postulate is generally
correct, it would be a major step toward understanding the trace chemistry
of the atmosphere.

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